

Tannin-boron wood preservatives.

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ABSTRACT

Tannin-boron wood preservatives are alternative products to replace water-borne formulations based on copper. Interesting results in protection against fungus (*pycnoporus sanguineus*) were achieved with formulations based of 20% tannin solutions containing boric acid (Thevenon *et al.* 2009).

In this paper two upgrades are introduced: extension of preservation properties to softwood species (scots pine) and analysis of the side-properties achieved after treatment.

A detailed study on tannin penetration in beech and scots pine is presented. Microscope analysis demonstrates that impregnation in scots pine have two preferential directions: Longitudinal through tracheids and radial through parenchyma rays, while in beech the liquid penetrates the wood cell mainly longitudinally through large and easy accessible vessels.

Commercialization of exterior-door wood preservative will be also dependent on the side-properties derived from the treatment. For this reason, properties such as mechanical resistance and behavior against fire have been investigated. The mechanical tests have shown a strong increasing of compression resistance and surface hardness for beech and scots pine samples.

The tests against fire have been monitored considering ignition, flame and ember time. A broad positive effect on fire-repellence is shown when wood is treated with tannin-boron formulations.

1. Introduction

Since creosote has been considered extremely polluting, the market of water-borne wood preservatives has been dominated by heavy- metal based formulations (CCA, ACQ, ACZA). Nowadays, in wood preservation, more natural products alternative to the commercially available are required. The use of boron combined with tannin resins seems to be a really promising alternative.

1.1. Boron

Boron compounds like boric acid, borax or disodium octaborate tetrahydrate have proved their efficiency as wood preservatives for many years. These compounds have demonstrated to be highly toxic to fungi and insects (including termites). (Lloyd, 1997; Grace and Yamamoto, 1994). The high solubility in water of these compounds, allow them to be introduced in wood by conventional methods such as dipping and diffusion or vacuum-pressure treatments (Byrne and Morris, 1997). Usually, many efforts in research are spent to get solvent-free solutions and in the case of boron its water solubility is definitely a great advantage. This property, however, makes them unsuitable for weathering because boron compounds are easily leached out. Thus, boron treated wood is useless for outdoor applications without any additional protection (Peylo and Willeitner, 1997). Nevertheless, boron compounds have relatively low toxicity for human beings (Teshima *et al*, 2001) and for some animal species (Maier and Knight, 1991). As an active ingredient of wood preservative formulations, boric acid is still eco-toxically and environmentally acceptable.

Several different methods have already been tried to decrease the leachability of boron from wood and to use them for exterior and/or ground contact applications (Kartal *et al*, 2003).

1.2. Tannin

Polyflavonoid or condensed tannins are natural compounds present in many plants. These compounds are used by plants as natural preservatives against biological attack by insects, fungi and bacteria (Hagerman *et al*, 1998). Due to their hydroxy-aromatic chemical composition, flavonoids are radical scavenger and hence they can be used as UV-ray protective. Furthermore the high reactivity of these compounds with hardeners (formaldehyde, hexamine, etc.) was the key-feature for their development in wood adhesives (Pizzi *et al*, 1995; Pichelin *et al*, 1997). In these processes the chemical condensation between flavonoids and aldehydes, is catalyzed by temperature and this kind of activation allows the polymerization to take place “on site”.

The use of mimosa (*Acacia Mearnsii* formerly *Mollissima* De Wildt) tannin extract combined with hexamethylenetetramine (hexamine) as hardener presents two advantages. First is possible to anchor the tannin in wood with a recognized non-formaldehyde-emission compound (Pichelin *et al*, 2006, Kamoun *et al*, 2003) and then the boron can be complexed by the flavonoids giving enough mobility to be active but not enough to be leached out (Pizzi and Baecker, 1996; Thevenon *et al*, 2009).

The cross-linked polymer improves the waterproofing of the treated wood and hence its durability.

The combination between boron and tannin network has already shown surprising results in EN113 tests that have been done against *Pycnoporus sanguineus* (strain CTFT 270) (Fig. 1).

<u>Impregnation Solution</u>	<u>Weight loss (%)</u> <u>Control</u>	<u>Weight Loss (%)</u> <u>Treated Samples</u>
10% Tannin	43,3	33,2
20% Tannin	47,4	25,4
10% Tannin + H ₃ BO ₃	45,7	3,42
20% Tannin + H ₃ BO ₃	41,2	3,95
10% Tannin + H ₃ BO ₃ Leached	35,5	1,69
20% Tannin + H ₃ BO ₃ Leached	36,3	1,74

Figure 1- Table of weight loss for treated samples exposed to EN 113 biological test.

The most interesting aspect was that even after leaching the preservation properties of tannin-boron treated samples were surprisingly high (Thevenon *et al*, 2009).

The follow-up of this research is divided in two big issues that are both reported in this paper. First topic is the applicability of this innovative formulation for other kind of wood (softwoods), and the second is the evaluation of the side-properties achieved after the preservation treatment.

2. Material and methods

2.1. Wood Impregnation

Sapwood of scots pine (*Pinus Sylvestris*) and beech (*Fagus Sylvatica*) pieces of different size (tailored in accordance with the test to undergo) have been dried for at least one week at 104°C. These samples have been placed into a desiccator and 8mbar vacuum has been applied to remove most of the air trapped in the wood cells. Afterwards the desiccator has been filled up with the impregnation solution and pressure has been slowly increased up to environmental pressure. In accordance with the different kinds of wood treated and with the viscosity of the impregnation solution, different vacuum and impregnation times have been applied.

The weights of the wood samples have been gathered before and after the treatment to evaluate the penetration of the impregnation solution.

The wet samples have been kept for at least 12 hours at 104°C to let the tannin-hexamine resin harden and then they have been stored in a climatic chamber at 12% moisture content for at least one week before testing.

Tannin impregnation solutions were prepared with 10% to 30% w/w of mimosa extract. The pH of these solutions was always corrected with a NaOH 50% solution to a pH of 9. 6% by weight of hexamine as crosslinking agent was added. Boric acid and phosphoric acid (5% by weight) were also added for the tests against fire.

2.2. Microscope Analysis

Scots pine and beech samples of 20 x 10 x 10 mm treated with a 20% tannin-hexamine resin have been analysed. Before cutting, the impregnated samples have been softened by boiling. They have been immersed into a flask of water with few drops of glycerin (defoamer) and were boiled under reflux for different times according with the hardness of the wood species. The slices were then cut under wet conditions in the three anatomical directions (transversal, radial and tangential) with a Leica SM 2000 R microtome to a thickness of 10 µm.

2.3. Compression tests

60 x 20 x 20 mm pieces of scots pine and beech treated and untreated have been tested in compression following the standard DIN 52185. The samples have been tested using a Zwick /Roell Z 250 universal testing machine with a speed of 2 mm/min.

2.4. Hardness tests

Hardness of scots pine and beech samples have been tested according to the Brinell test EN1534. The tests have been done with a specific machine for Brinell hardness “emco-test automatic”.

2.5. Short time fire exposition test

50 x 25 x 15 mm samples of scots pine and beech have been tested against fire. The larger surface (radial) has been exposed to 100% oxidant flame of a Bunsen burner. The distance

between Bunsen burner and sample has been kept fix at 2 cm and the burning times have been controlled with a stop-watch. Ignition, flame and embers time have been recorded for each sample. Ignition time is the minimum exposition time necessary to let the flame self-burn.

The flame time measures how long the sample keeps the flame after 2 and 3 minutes of continued exposition. Embers time measures how long it takes the sample to completely extinguishes (no more red spots, no more fumes).

3. Result and discussions

The effectiveness of wood preservatives is definitely dependent from the chemical substances that are involved in the protection towards fungus, bacteria, and insects. The use of boron based preservative instead of heavy metal based formulations will depend mainly from the performances in durability of both. It has already been proved that boron based preservatives have strong activity against fungus and bacteria but their durability does not depend exclusively on this parameters.

Durability is the most important characteristic in wood preservation and it depends on several other aspects such as leaching, fire and scratch resistance.

3.1. Wood penetration

Wood penetration is a side property of every formulation for preservatives. Easily penetrating products allow to protect the wood structure more in depth. Massive treated wood maintains its properties longer and can better resist the attack from external agents (rain, sun, biologic attacks, fire and scratches).

Penetration consists of two aspects: the raw uptake of preservative and the amount of solid resin released.

These two parameters are dependent on the physical and chemical features of the preservative, the impregnation conditions applied and the anatomy of the wood species treated.

The figure shown below (Fig.2) reports the uptake trends in tannin based preservative penetration and solid resin released in beech and scots pine with fixed impregnation conditions.

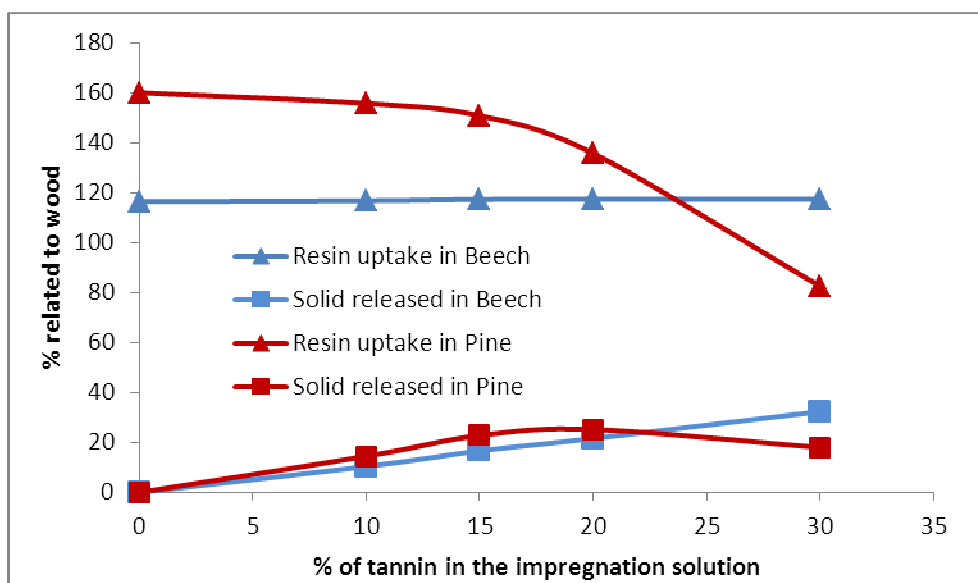


Figure 2- Penetration and solid releasing trend for tannin solutions in beech and scots pine.

It can be observed that the tannin solutions with up to 30% s.c. can easily penetrate the beech samples and the impregnation can be considered complete. Tannin solutions of 40% solid content have high viscosity (around 400 cp) and hence they are not applicable as massive/solid wood preservative.

The penetration of beech samples reported in the graphic can be obtained applying 30 minutes of 8 mbar vacuum and 2 hours of impregnation time at room pressure. The formulation releases a proportional amount of solid resin and then it is easily possible to regulate the amount of solid preservative required for each application.

Sapwood of scots pine is much more reticent to be impregnated by tannin based formulations. Even when the impregnation conditions applied are more severe (Vacuum time= 2h; Impregnation time= 24h) there is a significant decrease of penetration (15%) when 20% of tannin solutions are applied (Fig. 2). The solid content of 20% of tannin in the impregnation solutions represents the top threshold for the applicability of tannin formulations in scots pine.

However, it has to be underlined that the penetration obtained with diluted solutions of pine are also satisfactory because the released amount of solid preservative is still slightly higher than the respective value for beech. This observation means that in scots pine good performances can be achieved even when lower amounts of resins are applied.

Considering that scots pine and beech treated with the same formulation, at the same impregnation condition are not equally impregnated; the only parameter that affects penetration is their wood anatomy.

Porous wood like beech presents very large vessels homogenously distributed in the whole wood structure. Through these 40-90 μm vessels, which are already used by the living plant to transport water, the passage of liquid is easy. Good impregnations are achieved even applying smooth impregnation conditions (Fig.3a).

Conversely, scots pine has a closer structure and the liquid hardly penetrates the wood sample. The impregnation happens in two directions: Longitudinal penetration is ensured by tracheids cells while radial penetration goes through parenchyma rays (Fig. 3b).

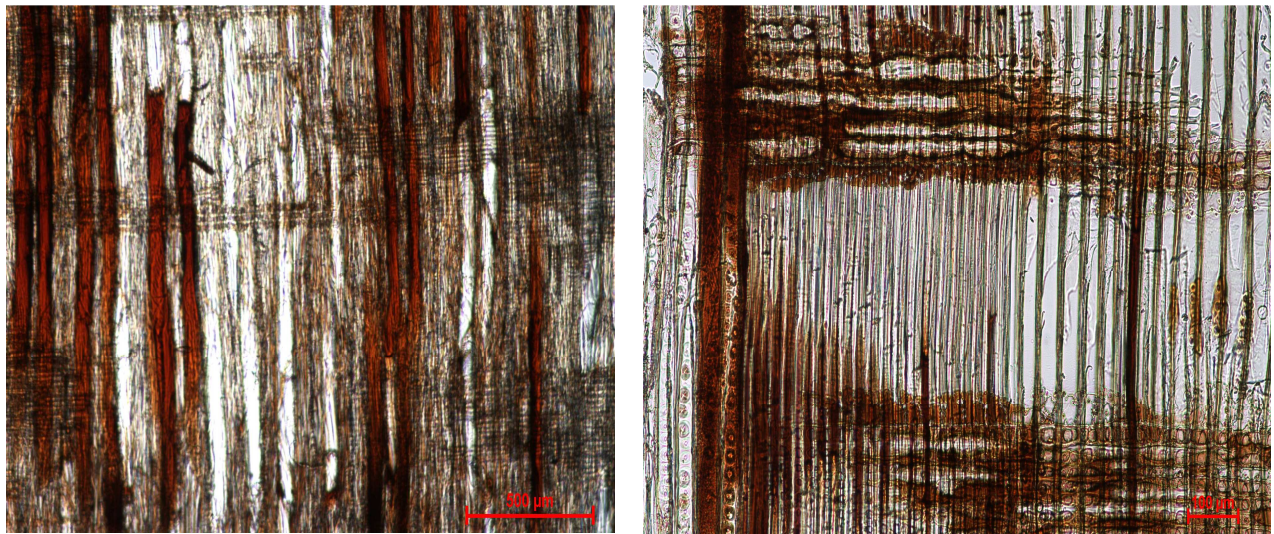


Figure 3- Microscope overview of radial sections of beech and scots pine impregnated with 20% tannin solution.

The wood tracheids connected to parenchyma rays are impregnated and it appears that in latewood the penetration is easier.

In terms of dimensions, it is possible to observe that parenchyma's ray have a diameter of 150-200 μm and hence there is no efforts for tannin to penetrate. Conversely, the vertical penetration is regulated by pits membrane and is not easy to foresee. These results are also supported by the penetration studies of these wood species made by Scholtz (Scholz *et al*, 2010).

In consideration of these observations, it is always better to use diluted impregnation solutions for scots pine samples. This shrewdness allows a deeper and more homogenous distribution of the wood preservative with less drastic impregnation conditions.

A primary role in wood penetration is played by the impregnation solutions. Low viscosity tannin solutions penetrate easier in wood. Thus, low concentration of tannin and low polymerization degree are preferred. These conditions are mandatory for the correct impregnation of wood

species that are not easy to penetrate. In some extreme case of penetration (e.g. spruce), heat can be applied. Temperature, indeed, has a double effect: at the beginning it decreases the viscosity and activates the tannin-hexamine crosslinking process and so the shelf-life of the formulation decreases fast.

3.2. Mechanical Properties

Beech and scots pine samples assume a different aspect after tannin-boron treatment.

The most apparent changes are the darker color, the smoother surface and the more rigid aspect. The presence of the tannin-hexamine resins in the wooden structure gives a more consistent aspect to the whole structure.

The quantification of this mechanical property is fundamental to consider the tannin-boron formulation applicable to wood for exterior grade applications. For this reason, compression test and hardness measurements have been done.



Figure 4- Compression strength in function of tannin impregnation.

Fig. 4 represents the percentage of strength performance increase in compression resistance when tannin solutions are cross-linked into the wooden structure.

The most immediate result is the general increase of resistance. In case of beech, the penetration of the tannin formulation is proportional to the concentration of tannin in the impregnation solution. This information suggests a homogeneous distribution of the resin and explains why the mechanical properties are proportionally increased. This increasing is significant and takes even more value considering that beech is around 70% more resistant to compression than scots pine.

Also for treated scots pine samples the resistance to compression increases. The solution of 10% of tannin penetrates deeply and produces a homogeneous distribution of the network after curing. In this case the mechanical resistance achieved is really high (around 35%). Unfortunately, when the viscosity of tannin becomes slightly higher, the penetration in scots pine is not complete and the distribution of the resin is less homogeneous. The mechanical resistance is still higher, but there is not proportionality between tannin used and strength increase.

Eventually, scots pine can be also reinforced with a tannin-hexamine formulation, but in these cases lower concentrations are suggested.

Anyways, this increase is always significant and this treatment can be considered not only as an innovative and eco-friendly solution to increase durability, but also as a method to get the wood more resistant for building construction.

Brinell hardness investigates the surface properties of the wood samples. Fig. 5 reports on the trend in surface hardness for beech and scots pine in relation with tannin-hexamine treatments.

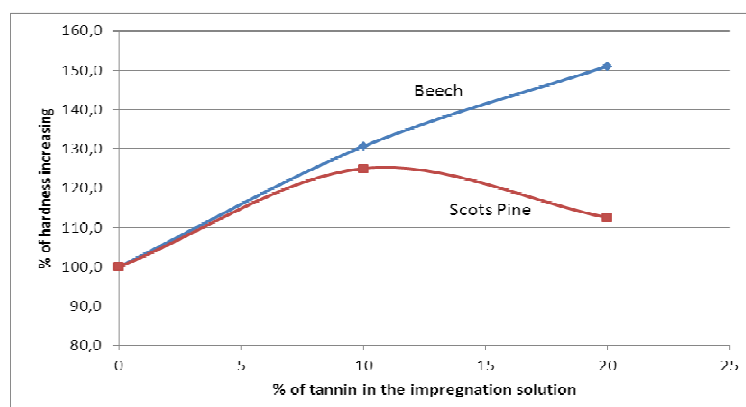


Figure 5- Percentage of Brinell hardness increasing in function of tannin impregnation.

Even for this surface phenomenon, the proportionality between hardness and tannin amount in the impregnation solution is respected only when the penetration is complete. For this reason the treatment of scots pine with a too concentrated (20%) solution of tannin does not give the expected results. Notwithstanding that the hardness is a surface property, the overall structure is stressed and a better hardness is achieved when the samples are homogeneously filled. Overall, the treated samples always increase their hardness after tannin impregnation treatments and their resistance to scratch is then upgraded.

3.3. Fire Properties

Another important question for exterior grade wood preservatives is their behavior against fire. This characteristic is always studied when the samples have big dimensions to evaluate their mechanical stability. Unfortunately, big dimension autoclaves are required to impregnate structural wood pieces. Thus, to achieve comparative results, easier lab-scale test have been conducted. Comparative results for short time exposition tests are reported in Fig. 6.

Parameter	Scots Pine					Beech				
	Ignition Time (s)	Flame Time	Flame Time	Ember Time	Ember Time	Ignition Time (s)	Flame Time	Flame Time	Ember Time	Ember Time
		2 min (s)	3 min (s)	2 min (min)	3 min (min)		2 min (s)	3 min (s)	2 min (min)	3 min (min)
Untreated	12	140	120	4	3,9	12	255	310	9	13
10% Tannin	75	35	110	2,5	6	40	60	180	2,5	11
20% Tannin	100	22	80	2,5	7	75	15	80	3,5	10
20% Tannin + Boric Acid	110	25	31	0,8	1,5	60	25	90	0,8	3
20% Tannin + Phosphoric Acid	120	15	27	0,9	2,5	65	22	80	1	2,8

Figure 6- Table of short time fire tests of scots pine and beech.

Analyzing this table it appears that the effect of tannin decreases the burning properties of samples. The ignition time significantly increases and the flame extinguishes faster than for the respective untreated sample.

The application of more concentrated tannin solutions releases more tannin and hence it further increases the fire resistance properties.

When 20% tannin solutions are applied, the pieces are at least 6 times more difficult to light on and once they are exposed to 2 minutes of direct flame they stop keeping the flame at least 6 times before. Also the ember time decreases but in this case the data have to be more carefully interpreted. After the flame is extinguished the red spots glow very slowly when the wood is treated

with tannins. When the exposition is longer (3 min) the flame penetrated deeper into the sample and especially for pine this imply a longer ember time.

It has to be reported that especially in the case of beech samples, the hardened tannin resin modifies the elasticity of the structure. When treated beech is undergone for a long time (>3 minutes) to a flame it has the tendency to suddenly break up.

The use of inorganic compounds in the formulation increases the fire resistance properties of the samples. Particular activity is pointed out for the complete extinguish of the sample which becomes at least twice faster.

This flame retardant action of tannin-furanic copolymer was already known (Tondi et al, 2009). The fire properties of tannin-hexamine copolymers have never been tested before and these preliminary tests can suggest some interesting information, also for the wood composite industry.

The tannin-boron combination, which has already shown very good properties in wood preservation, seems to be really interesting also for its flame retardant properties.

4. Conclusions

Tannin boron wood preservatives kept the attention of the scientific community for their impressive properties as fungicide for beech samples. The follow up of this project was to extend these features to other wood species and to study in deep which were the side-properties of this treatment.

In this work it has been seen that this technology can be applied to scots pine working with more diluted solutions and taking care of the anatomic characteristics to avoid low penetration.

Mechanical tests have shown that for beech and scots pine, the treatment increases the compression resistance and hardness of the samples.

Treated beech samples can improve their mechanical properties up to 15% in compression resistance and up to 50% in hardness with solutions containing 20% of tannin.

For scots pine the best improvements are achieved when 10% tannin solutions are applied. In these samples, compression resistance increases of 35% while hardness increases of around 25%.

Impregnated wood samples exposed to direct flame have shown to be much more fire resistant. Once the wood samples are treated with tannin, the ignition time becomes much longer and the flame extinguish time much shorter. The use of boron and phosphoric acid then break down the embers time and complete the characteristics of this fire resistant formulation.

All these considerations keep the interest open for the up-scaling of this technology based on tannin-boron synergies.

Before extending this promising technology to a semi-industrial scale, more virulent biological tests (e.g. termites), stronger condition leaching tests and artificial ageing tests are planned.

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